

# Clear Evidence of Reptation in Polyethylene from Neutron Spin-Echo Spectroscopy

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(Received 27 January 1998)

The dynamic structure factor  $S(q, t)$  of polyethylene (PEB-2) was measured by neutron spin echo in the Fourier time range of  $t = 0.3$ –175 nsec and for momentum transfers  $q$  between 0.05 and  $0.145 \text{ \AA}^{-1}$  to test the validity of competing phenomenological theories of relaxation in polymer melts. Previous spin-echo experiments limited to  $t < 25$  nsec were equally well described by a variety of models. This ambiguity has now been lifted, and the experiment clearly favors the reptation model, showing that the dominant relaxation mechanism in entangled linear polymers is via reptation. [S0031-9007(98)06468-0]

PACS numbers: 61.25.Hq, 61.12.-q, 83.20.Fk

The dynamics of a dense polymeric system is dominated by entanglement effects which give rise to a temporary network of topological constraints severely restricting the motional degrees of freedom of each chain [1]. The reptation hypothesis of de Gennes [2] is the most successful phenomenological approach to date for describing the dynamics of long polymer chains [3], although a strict experimental test on a molecular level is still missing. Recent claims to have unambiguously observed reptation by interdiffusion experiments [4] were disputed later by theoretical calculations [5]. These calculations show that the Rouse [6,7] and mode-coupling models [8], which both lack the particular features of reptation, lead to similar interdiffusion profiles. Thus the question remains whether reptation is indeed the dominant relaxation mechanism in entangled linear-chain systems.

The concept of reptation is particularly appealing in its simplicity [2,7,9]: The motion of an individual polymer is postulated to be restricted by the surrounding chain conformations within a tube defined by the overall chain contour. During the lifetime of this tube ( $\tau_d$ ), any lateral diffusion of the chain is thus quenched. Initially, the chain relaxes freely until the mean-squared displacement becomes comparable to the tube diameter  $d$ . After a time  $\tau_e = N_e^2/(\pi^2 W)$ , the chain has explored the extent of its lateral confinement. Here,  $N_e$  is the number of segments of length  $l$  spanning a distance  $d$  ( $d^2 = l^2 N_e$ ), and  $W$  is the microscopic attempt frequency, or Rouse rate. For longer times, until  $\tau_R = N^2/\pi^2 W$  ( $N$  is the total number of chain segments), the chain's modes may relax only along the tube profile (*local reptation*). Thereafter, a longitudinal creep along the tube (*reptation*) is possible. The time scale for such collective motion is clearly much larger than the transverse relaxation (the reptation time  $\tau_d \sim N^3$ ). The result is a *plateau* or stagnation in the decay of the single-chain correlation function in time, due to the confinement of the chain within its tube. Ultimately, for times longer

than the reptation time  $\tau_d$ , normal diffusive behavior is expected.

The physical quantity which is sensitive to these density fluctuations is the single-chain dynamic structure factor  $S(q, t)$ , which is the Fourier transform of the real-space pair correlation function ( $q$  is the wave vector). De Gennes [10] has formulated a tractable expression, valid for times larger than  $\tau_e$ , i.e., once the confinement effects are felt. In the reptation picture, for  $t > \tau_e$  and for wave vectors much larger than the inverse of the chain end-to-end distance  $R_0$  (i.e.,  $qR_0 \gg 1$ ) the single-chain dynamic structure factor is [11]:

$$\frac{S(q, t)}{S(q, 0)} = \{1 - \exp[-(qd/6)^2]\} \exp(t/\tau_e) \operatorname{erfc}(\sqrt{t/\tau_e}) + \frac{8}{\pi^2} \exp[-(qd/6)^2] \sum_{\text{odd } n} \frac{1}{n^2} \exp(-n^2 t/\tau_d). \quad (1)$$

This equation describes the decay of correlations due to *local* reptation (first term) crossing over reptational diffusion (second term), where the two time scales  $\tau_e$  and  $\tau_d$  are given by

$$\tau_e = \frac{36}{Wl^4 q^4}; \quad \tau_d = \frac{3N^3 l^2}{\pi^2 W d^2}. \quad (2)$$

Since the ratio between these time scales goes with  $N^3$ , a well pronounced plateau is expected for long polymers at intermediate times  $\tau_e < t < \tau_d$ . Such a plateau is the signature of the confined motion due to entanglements (*independent* of the reptation hypothesis). The single-chain dynamic structure factor  $S(q, t)$  can be measured via neutron spin echo (NSE) spectroscopy on a dilute mixture of fully protonated chains within a background of deuterated, but otherwise identical, chains. A neutron scattering experiment is thus sensitive to the single-chain correlations as a result of the scattering length contrast between the protonated (i.e., labeled) polymer and the deuterated background.

NSE spectrometry directly measures  $S(q, t)$  [12], where typically the highest attainable Fourier times have been limited to about 30–50 nsec. On this time scale, NSE has already played a crucial role in helping to understand the dynamics of polymeric systems [9,13–17], where, for example the existence of an entanglement length scale in a linear polymer has been proven [13]. However, until now, NSE has not been able to separate the reptation model from other phenomenological entanglement theories, such as the rubberlike model of des Cloizeaux [18], where the polymer is assumed to be spatially fixed at transient (but long-lived) cross-links, and undergoing Rouse-relaxation in between. Also under consideration is the model of Ronca [19], which is a generalized Rouse model where the influence of the neighboring chains is approximated via a memory function of an elastic medium. Finally, a recent model of Chatterjee and Loring [20] has appeared, where the entanglements are treated as fluctuating obstacles hindering individual chain relaxation. All these models are more or less consistent with the existing NSE data, despite representing different basic relaxation mechanisms.

The inability to clearly distinguish between these models arises from the fact that the longest attainable Fourier time for existing NSE spectrometers is insufficient to reach far enough into the plateau region where the differences between theories become apparent (Fig. 1). In addition to this, a recently developed “first-principles” mode-coupling theory [8] does not support the concept of

reptation. Since this is a microscopic theory, it seriously challenges the idea that reptation is the principal relaxation mechanism. Addressing this issue through Monte Carlo or molecular dynamics simulations is exceedingly time consuming, and the investigation of reptation through simulations finds itself in an analogous situation as the early NSE investigations [21]. Thus, without the development of a NSE spectrometer capable of exploring a substantial part of the plateau region, this issue is unlikely to be easily resolved.

A significant step forward has recently been made through the development of an instrument (IN15 at the Institut Laue-Langevin [22]) capable of exceeding Fourier times of 300 nsec (Fig. 2). This greatly surpasses the previous limit of (at most) 30–50 nsec for existing instruments and opens up the possibility for exploring dynamic phenomena which were previously unobservable. By sufficiently extending the upper limit in  $t$ , one is now able to reach far into the plateau regime and look for clearer signatures of reptation.

The same polyethylene (PEB-2) sample of molecular weight  $M_w = 36\,000$  as used in previous NSE experiments [16] was remeasured at  $T = 509$  K on IN15. This system is well suited for studying the effect of entanglements. It is a linear polymer, stable at high temperatures. PEB-2 has a high segmental mobility ( $Wl^4 = 7.0 \pm 0.7 \times 10^{13} \text{ \AA}^4/\text{s}$  at 509 K) and should exhibit a well defined plateau ( $N_e = 140$ ,  $N = 2570$ ) [14]. From the previous NSE measurements the tube diameter was

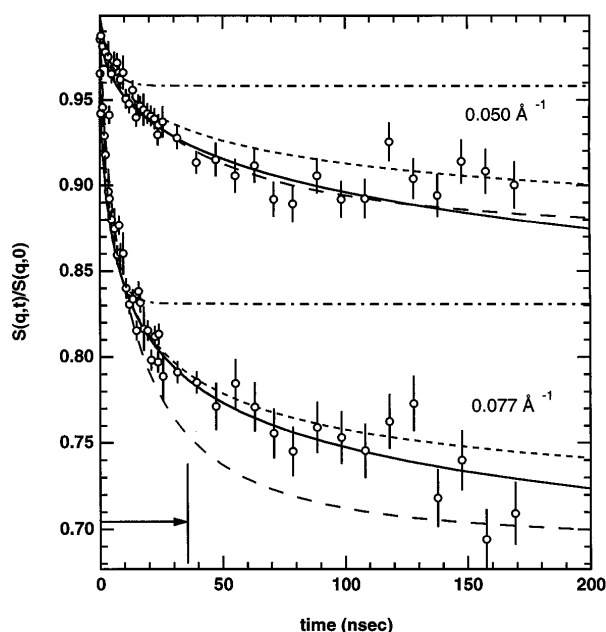


FIG. 1. Plot of  $S(q, t)$  vs  $t$  at  $q = 0.050$  and  $0.077 \text{ \AA}^{-1}$ , with a comparison between the predictions of reptation (solid lines), local reptation (dotted lines), the model of des Cloizeaux [18] (dashed lines), and the Ronca model [19] (dot-dashed lines). The vertical line and arrow indicate the upper Fourier-time limit of previous experiments.

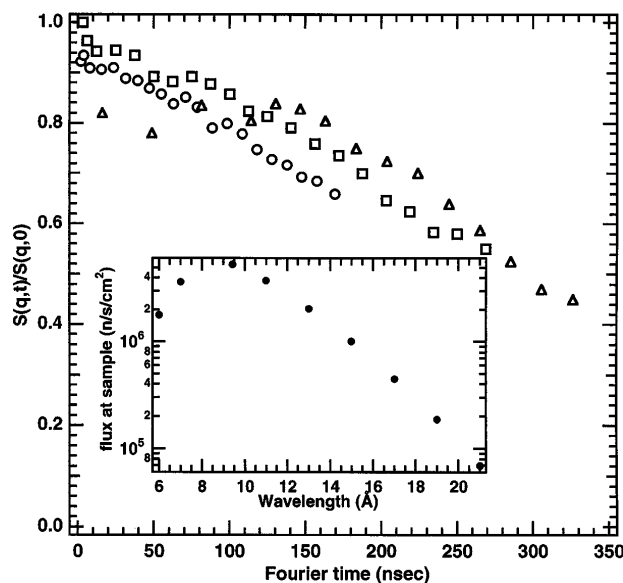


FIG. 2. Normalized echo amplitude for an elastic, 35 mm diameter (graphite) scatterer vs Fourier time. The circles, squares, and triangles represent the spin echo “resolution” for an incident neutron wavelength of 15, 17.5, and 19 Å, respectively ( $\Delta\lambda/\lambda = 15\%$ ), and a momentum transfer of  $q \approx 0.06 \text{ \AA}^{-1}$ . The inset shows the incident flux on the sample vs wavelength under the experimental configuration used for this investigation.

evaluated to be  $43.5 \text{ \AA}$ , implying a crossover time of  $\tau_e \approx 5 \text{ nsec}$ , using  $l^2 = 13.05 \text{ \AA}^2$  (Ref. [9]). To increase the dynamic range we made separate measurements at two different neutron wavelengths. This takes advantage of the strong  $\lambda$  dependence of the Fourier time ( $t \sim \lambda^3$ ). Wavelengths of  $\lambda = 8$  and  $15 \text{ \AA}$  with a  $\Delta\lambda/\lambda = 15\%$  (FWHM) were used to achieve a measurement range of  $0.3 < t < 170 \text{ nsec}$ . Measurements with longer wavelengths were not possible due to the low counting rates. The spin-echo amplitude was corrected for instrumental resolution, which was qualitatively similar to the resolution depicted in Fig. 2. The other measurement details are identical to those described by Richter *et al.* [16].

The experimental results and fits using Eq. (1) as well as the model of des Cloizeaux [18] and Ronca [19] are shown in Figs. 1 and 3. The entanglement distances emerging from the different fits are given in Table I. The larger uncertainties in the data for increasing  $q$  are due to the fact that both the scattering intensity and the normalized spin-echo amplitude decrease with increasing  $q$ . The fits were done simultaneously for all  $q$  and  $t$ . It is apparent that these data *clearly* favor the reptation model. To our knowledge, the reptation model is the only model for which the dynamic structure factor has been calcu-

lated and which is in quantitative agreement with these NSE data: On the one hand, the models of Ronca [19] (see Fig. 1) and des Cloizeaux [18] (see Fig. 3) produce a plateau which is too flat. On the other hand, the model of Chatterjee and Loring [20] relaxes too quickly, which we do not reproduce here as it is sufficiently evident from their Fig. 3 in Ref. [20], for example.

In Fig. 3 it is apparent that the model of des Cloizeaux also suffers from an incorrect  $q$  dependence of  $S(q, t)$  in the plateau region, which is most apparent at the highest  $q$  measured. It is important to note that the fits with the reptation model were done with only one free parameter, the entanglement distance  $d$ . The Rouse rate  $W$  was determined earlier through NSE data taken for  $t \ll \tau_e$  and the rest are fixed from other measurement techniques [9]. With this one free parameter, we find quantitative agreement over the *whole* range of  $q$  and  $t$  using the reptation model with  $d = 46.0 \pm 0.1 \text{ \AA}$ . The tube diameter deduced here is essentially unchanged from the previous NSE data for  $t < 20 \text{ nsec}$  ( $d = 43.5 \pm 0.7 \text{ \AA}$ ; Ref. [9]), where it was already found to agree with the tube diameter deduced from the plateau modulus in rheological measurements ( $d = 42 \text{ \AA}$ ; Ref. [23]).

One might ask if these data are actually sensitive to the reptational diffusion via a creeping motion along the tube, or if only *local reptation* is important on this time scale. Local reptation effectively corresponds to  $\tau_d = \infty$ , and indeed a difference between global and local reptation becomes apparent only at sufficiently small  $q$  (see Fig. 1). Only then does the weight of the first term in Eq. (1) become sufficiently weak to make the effect of reptational diffusion visible on the time scale measured. Fitting  $\tau_d$  as a free parameter, rather than fixing it to the tube diameter  $d$  via Eq. (2), is a direct measure of the reptation time. Doing this gives  $\tau_d = 130 \pm 36 \mu\text{sec}$ . Considering the uncertainty, this is consistent with the value of  $77.4 \pm 0.2 \mu\text{sec}$  deduced from Eq. (2). This represents the first estimate of the reptation time based on NSE measurements.

In summary, the quantitative experimental technique of NSE spectroscopy has seen an unambiguous signature of reptation in a flexible linear polymer. The data now cover a substantial region of the time domain where the reptation concept is in principle applicable. Compared with other phenomenological entanglement models, reptation is now the only approach that provides a consistent description of *all* the NSE data. This is

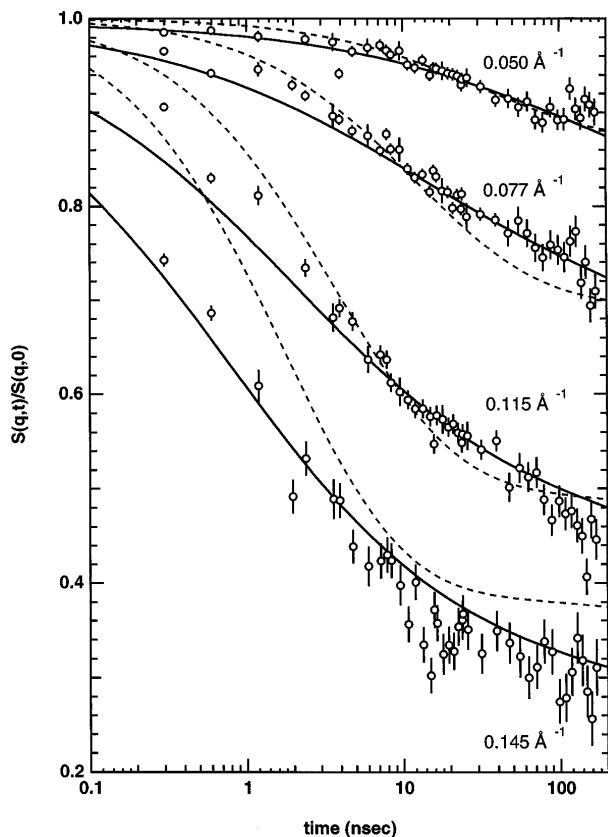


FIG. 3. Semilog plot of  $S(q, t)$  vs  $t$  for various  $q$ . The solid lines are the fit of the reptation model [Eq. (1)]. The dashed lines are a fit using the model of des Cloizeaux [Eq. (27) of Ref. [18]].

TABLE I. Fit results for the entanglement distance  $d$  for various models. The reduced  $\chi^2$  is also indicated.

Model	Ref.	$d$ ( $\text{\AA}$ )	Reduced $\chi^2$
Reptation	[10]	$46.0 \pm 0.1$	3.03
Local Reptation	[10]	$46.5 \pm 0.1$	3.21
des Cloizeaux	[18]	$59.8 \pm 0.2$	7.19
Ronca	[19]	$47.4 \pm 0.1$	12.2

compelling evidence that reptation is indeed the principle relaxation mechanism in entangled linear-chain systems. A direct test of whether the current mode-coupling theory for linear polymers is compatible with these data can only really be done once the theory has considered the full space-time development of the motional processes which lead to the dynamic structure factor, instead of concentrating solely on the temporal aspect.

We wish to thank P. Giraud and J.F. Barthélemy for technical assistance. P.S. is grateful for stimulating discussions with B. Alefeld, G. Ehlers, C. Hayes, and F. Mezei, during the final stages of the instrument development.

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